## Simple Synthesis of Uniformly Small Gold Nanoparticles for Sensitivity Enhancement in Colorimetric Detection of Pb<sup>2+</sup> Ions by Improving Their Reactivity and Stability

Yujiao Xiahou,<sup>a</sup> Peina Zhang,<sup>a</sup> Jin Wang,<sup>a</sup> Lihui Huang<sup>b</sup> and Haibing Xia\*<sup>a</sup>

<sup>a</sup>State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, P. R China;

<sup>b</sup>School of Environmental Science and Engineering, Shandong University, Jinan, 250100, P. R. China. **Equation S1**. Possible equations involved during the detection of  $Pb^{2+}$  ions via 2-ME/S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-TB-Au NP sensors and detailed description of possible reaction process.

(1) 
$$4Au^0 + O_2 + 2H_2O + 8S_2O_3^2 \rightarrow 4Au(S_2O_3)^3 + 4OH^2$$

In the existence of  $O_2$ , the dissolved oxygen gas served as an oxidant, a thiosulfate ligand will gain partial negative charge after attachment to Au NPs surface. In the suitable alkaline environment (pH 10), when the obtained Au NPs reacted with  $S_2O_3^{2-}$  ions in solution,  $S_2O_3^{2-}$  ions act as monodentate ligands via the terminal sulfur atom, establishing strong  $\sigma$  bonds with gold ions that are stabilized by  $p\pi$ -d $\pi$  back-bonding,<sup>1</sup>  $S_2O_3^{2-}$ -Au<sup>+</sup> complexes were formed immediately on the Au NP surfaces.<sup>2-4</sup> Thus, the average size of Au NPs decreased.<sup>5</sup>

(2) 
$$Au(S_2O_3)_2^3 + 2(2 - ME) \rightarrow Au(2 - ME)_2^2 + 2S_2O_3^2$$

Since that the stability of Au(I) complexes are different from diverse ligands: SH<sup>-</sup> >  $S_2O_3^{2^-.6}$  Parts of the prepared  $S_2O_3^{2^-}$ -Au<sup>+</sup> complexes rapidly dissolved to form 2-ME-Au<sup>+</sup> complexes in solution after adding 2-ME due to the high Au-S bond energy.<sup>1,7-10</sup> Thus, the formation of strong 2-ME-Au<sup>+</sup> complexes accelerated the leaching of the Au NPs in the  $S_2O_3^{2^-}$  ions leaching liquor.

(3) 
$$Au@Au(S_2O_3)^{3-}_2 NPs + Pb^{2+} \rightarrow Au@Pb NPs$$

Similar to a cyanide system, lead ions could react with gold to form lead alloys on the gold surface, accelerating gold dissolution in the thiosulphate system. At low Pb concentrations, the predominant species for Pb in the leaching region could be Pb(OH)<sup>+</sup> ions. AuPb<sub>2</sub> could also be present in the leaching region.<sup>3</sup> In a word, in the existence of  $S_2O_3^{2^-}$  ions, Pb<sup>2+</sup> ions reacts with gold to form AuPb<sub>2</sub> and AuPb<sub>3</sub> alloys or metallic Pb on the gold surface, resulting in a potential drop of the gold and, thus, an accelerated rate of dissolution.<sup>3,5,11</sup> As a result, the SPR extinction decreased dramatically coursed by the

formation of Au@Pb NPs, allowing quantitation of the Pb<sup>2+</sup> ions in the aqueous solution. As the concentration of Pb<sup>2+</sup> ions increasing, the extinction spectra value of Au@Pb NPs gradually decreased. **Scheme S1.** Schematic representation for possible mechanism of sensitivity enhancement. The variation in intensity of the extinction spectrum of Au NPs of big (a) and small size (b) before (black line) and after (red line) formation of Pb shell on their surfaces during the detection of Pb<sup>2+</sup> ions. The insets are the models of core-shell Au@Pb NPs formed, in which the size ( $r_1$ ) of Au core in (a) is bigger than that ( $r_2$ ) in (b) and the Pb thickness (d) is same.



**Figure S1.** Temporal evolution of the digital photos of the reaction solution during the growth of 3.5 nm Au-NP seeds recorded at different reaction times. The reaction times are 30 s (a), 1 min (b), 1.5 min (c), 2 min (d), and 3 min (e), respectively.



It was prepared as follows: 333  $\mu$ L of HAuCl<sub>4</sub> (25 mM) was added into a mixed solution containing 46.1 mL H<sub>2</sub>O, 3.2 mL sodium citrate (34.3 mM), 33.3  $\mu$ L TA (2.5 mM), and 333 uL Na<sub>2</sub>CO<sub>3</sub> (150 mM) at 70 °C. Fig. S1 (ESI†) shows the digital photos of the reaction solution recorded at different reaction times. The color of the reaction turned from transparent to dark gray (Fig. Sib, ESI†) instantaneously after the injection of HAuCl<sub>4</sub> solution, and then to brownish orange (Fig. Sie, ESI†) within a few minutes, indicative of the formation of very small Au NPs. The reaction solution was boiled for another half hour with stirring to warrant the formation of uniform Au NPs. The reaction solution was cooled to room temperature for further use.

**Figure S2.** TEM image (a) and extinction spectrum (b) of 3.5 nm Au-NP seeds. The inset in Figure S2a is size distribution of the corresponding Au-NP seeds measured by means of DLS.



The size of as-prepared Au-NP seeds was determined by TEM and Dynamic light scattering (DLS) (Fig. S2a and the inset, ESI†). The extinction spectrum is narrow and symmetric, and the full width at half-maxima (FWHM) is also small (Fig. S2b, ESI†), both indicating the high quality of Au-NP seeds. By assuming that the amount of the HAuCl<sub>4</sub> used was completely consumed for the synthesis of Au-NP seeds and the shape of the resulting Au-NP seeds was spherical, the total particle number of as-prepared Au-NP seeds in the solution (about 3.8 × 10<sup>15</sup>) can be calculated by  $6m_{Au}/\pi\rho_{Au}D^3$ , where  $m_{Au}$  is the mass of Au (which is derived from the amount of HAuCl<sub>4</sub> used for the synthesis of Au-NP seeds),  $\pi$  (pi) is the ratio of the circumference of a circle to its diameter,  $\rho_{Au}$  is the density of Au, and D is the diameter of the Au-NP seeds (3.5 nm). Since the total volume of the solution is 50 mL, the particle number concentration is about 7.6 × 10<sup>13</sup> NPs/mL.

**Figure S3.** Extinction spectra (a to l) of the resulting Au NPs. The size of the Au NPs are  $5.5 \pm 0.7$  nm (a),  $6.9 \pm 0.7$  nm (b),  $7.7 \pm 0.8$  nm (c),  $8.5 \pm 0.8$  nm (d),  $8.9 \pm 0.8$  nm (e),  $10.6 \pm 0.8$  nm (f),  $11.6 \pm 0.6$  nm (g),  $12.6 \pm 0.9$  nm (h),  $14.3 \pm 1$  nm (i),  $15.1 \pm 1$  nm (j),  $16.7 \pm 1$  nm (k), and  $17.8 \pm 2$  nm (l), respectively. The resultant temperature are 70 °C (a to e), 85 °C (f to h), and 100 °C (i to l), respectively.



**Figure S4.** TEM images (a, b, d and e) of 14.3 nm Au NPs obtained at 85 °C (a) and (b) at 100 °C, and 8.8 nm Au NPs obtained at 70 °C (d) and at 100 °C, and their corresponding extinction spectra (c and f)



**Figure S5**. TEM images (a to i) and their corresponding extinction spectra (j) of Au NPs obtained at different pH values. The reaction conditions are same to those for synthesis of 17.8 nm Au NPs (Table 1) except the pH value of reaction media. The reaction pH are 3.5 (a), 6.5 (b), 7.2 (c), 7.7 (d), 8.5 (e), 8.9 (f), 9.1 (g), 9.4 (h), and 9.9 (i), respectively.



**Figure S6.** Extinction spectra of 6 nm Cit-Au NPs (a) and 5.5 nm TB-Au NPs (b) after being dispersed in NaCl solution of different concentrations. The concentration of the NaCl solution changes from 0 to 100 mM.



**Figure S7.** Extinction spectra of the different sizes of  $2-ME/S_2O_3^{2^2}-TB-Au_m$  NP sensors in the presence of different concentrations of PbCl<sub>2</sub> (o-10  $\mu$ M). The value of m is 15 (a), 10 (b), and 5.5 (c), respectively. The mass concentration of all Au NPs used in  $2-ME/S_2O_3^{2^2}-TB-Au_m$  NP sensors was the same. The concentration of  $S_2O_3^{2^2}$  ions was 1.0 mM. The concentration of 2-ME was 1 mM (a, m = 15), 1.3 mM (b, m = 10), and 0.57 mM (c, m = 5.5), respectively. The pH of test solution was about 10 by using TB solution (0.17 M).



**Figure S8.** Extinction spectra of the 2-ME/S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-TB-Au<sub>5.5</sub> NP sensor in the presence of different metal ions: Li<sup>+</sup> ions (a), Na<sup>+</sup> ions (b), K<sup>+</sup> ions (c), Mg<sup>2+</sup> ions (d), Ca<sup>2+</sup> ions (e), Sr<sup>2+</sup> ions (f), Ba<sup>2+</sup> ions (g), Cr<sup>3+</sup> ions (h), Fe<sup>3+</sup> ions (i), Co<sup>2+</sup> ions (j), Ni<sup>2+</sup> ions (k), Cu<sup>2+</sup> ions (l), Zn<sup>2+</sup> ions (m), Cd<sup>2+</sup> ions (n), and Pb<sup>2+</sup> ions (o), respectively. The concentrations of Pb<sup>2+</sup> ions and other metal ions were set as 50 nM and 10  $\mu$ M, respectively. The concentrations of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions and 2-ME were both 1.0 mM. The pH of test solution was about 10 by using TB solution (0.17 M).



**Figure S9.** Extinction spectra (a to d) and their corresponding histogram (e) of the 2- $ME/S_2O_3^{2^-}$ -TB-Au<sub>5.5</sub> NP sensor in the presence of high concentration of metal ions: Na<sup>+</sup> ions (a), K<sup>+</sup> ions (b), Mg<sup>2+</sup> ions (c), and Ca<sup>2+</sup> ions (d). Error bars represent standard deviations from ten repeated experiments. The size of the Au NPs in use is 5.5 nm. The concentration of Pb<sup>2+</sup> ions was set as 50 nM. The concentrations of other metal ions were set as 10  $\mu$ M, 20  $\mu$ M, and 50  $\mu$ M, respectively. The concentrations of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions and 2-ME were both 1.0 mM. The pH of test solution was about 10 by using TB solution (0.17 M).



**Figure S10.** HAADF-STEM image (a), HAADF-STEM–EDS mapping images (b and c), and their overlapped image (d) of the obtained Au@Pb NPs, cross-sectional compositional line profile (f) of one single Au@Pb NP (e). The size of Au NPs used is 5.5 nm. The final concentrations of Pb<sup>2+</sup> ions,  $S_2O_3^{2^-}$  ions, and 2-ME are 50 nM, 1.0 mM, and 0.57 mM, respectively. The pH of test solution was about 10 by using TB solution (0.17 M).



**Figure S11.** CV curves of GCEs modified by as-prepared Au NPs (black curve) and Au@Pb NPs (red curve) in 0.01 M  $N_2$ -saturated HClO<sub>4</sub> aqueous solution at room temperature. The sizes of NPs are 5.5 nm (A) and 15 nm (B), respectively. The scan rates are 50 mV s<sup>-1</sup>.



**Figure S12.** (A) Extinction spectra of  $2-ME/S_2O_3^{2^2}$ -TB-Au<sub>5.5</sub> NP sensor in ultrapure water (a) and soil extract (b) and the linear relationships between the value of  $(Ex_0-Ex)/Ex_0$  of  $2-ME/S_2O_3^{2^2}$ -TB-Au<sub>5.5</sub> NP sensors and the logarithm of the concentration of Pb<sup>2+</sup> ions. The size of the Au NPs in use is 5.5 nm. The concentrations of  $S_2O_3^{2^2}$  ions and 2-ME were both 1.0 mM. The pH of test solution was about 10 by using TB solution (0.17 M).



The soil extract was diluted 10 times before testing. On the basis of the value of  $(Ex_o-Ex)/Ex_o$  and plot obtained (Fig. S12), the concentration of  $Pb^{2+}$  ions in soil extract is about 0.2 nM. Thus, the real concentration of  $Pb^{2+}$  ions in soil extract is about 2 nM.

**Table S1.** Summary of the figure numbers of TEM images of the corresponding Au NPs, the concentration of TB, the reaction pH, the actual sizes (diameter), size deviations, ellipticities of the resulting Au NPs obtained via one-pot, TB-assisted seeded growth, and the measured peak positions of their SPR bands.

Simple image	4a	4b	4C	4d	4e	4f	4g	4h	4i
TB [mM]	0.4	1,2	2	4	8	12	20	40	120
pН	3.5	6.5	7.2	7.7	8.5	8.9	9.1	9.4	9.9
Diameter [nm]	21.8	18.6	17.7	17.2	17.3	17.1	18.0	18.4	18.9
Deviation [%] <sup>a)</sup>	61.9	59.6	11.0	10.5	13.0	15.0	15.7	24.5	28.7
Ellipticity <sup>b)</sup>	1.29	1.24	1.05	1.05	1.07	1.13	1.13	1.25	1.28
SPR band position <sup>c)</sup>	521.3	519.5	517.7	517.7	517.7	517.9	518. 6	519.5	519.5

<sup>a)</sup> Standard deviation of the Au NP diameter; <sup>b)</sup> Ellipticity is estimated as the ratio of the major to minor axes; <sup>c)</sup> SPR band positions measured by UV-vis spectroscopy.

Table S2. Comparison of the	e performance for the detection of Pb <sup>2+</sup> ions.
-----------------------------	---

Method	Size	Materials	linear detection range	LOD	Reference
Colorimetry / Extinction spectra	14.2 nm	Au NPs	2.5 nM-1 μM	o.5 nM	5
Colorimetry / Fluorescence spectra	17 nm	Au NPs- DNAzyme	10 nM-2.5 µM	1.7 nM	12
Colorimetry / Absorbance spectra	14.2 nm	Au NPs	1-6 µM	40 nM	13
Colorimetry / Extinction spectra	15 nm	GA-Au NPs	10 nM-1 µM	N/A	14
Colorimetry / Absorbance spectra	13 nm	G/C-Au NPs	0.5-15 µM	1 µM	15
Colorimetry / Fluorescence spectra	N/A	rhodamine derivative	0.1-50 µM	25 nM	16
Colorimetry / Fluorescence spectra	N/A	T30695	10 nM - 1 µM	10 nM	17
Colorimetry / Extinction spectra	5.5/10/15 nm	Au NPs	0.1 nM - 5 μM	o.1 nM	This work

Sample	[Pb <sup>2+</sup> ] (nM)	Addition (nM)	Found (nM)	Recovery (%)	RSD (%)
Ultrapure water		7	5.8	82.9	9.9
		20	19.2	96.0	7.9
	0	30	30.0	100.0	6.7
	0	70	68.4	97.7	5.3
		200	203.7	101.9	4.1
		300	315.2	105.1	5.0
Soil extract		7	5.9	65.6	14.1
		20	19.6	89.1	7.9
		30	31.5	98.4	6.6
	2.0	70	68.4	95.0	5.3
		200	215.2	106.5	5.4
		300	330.4	109.4	6.3

**Table S3**. Recoveries for the detection of  $Pb^{2+}$  ions in ultrapure water and soil extract sample (n=10).

Treatment process of soil sample. All soil samples were air dried for 7 days, homogenized, and passed through a 2-mm sieve, and then stored at 4 °C before use. A soil sample (0.10 g) was weighed in an Erlenmeyer flask, and 100 mL of HNO<sub>3</sub> 1:1 (v/v) solution was added. The resulting mixture was heated on a hot plate to ~95 °C without boiling for 30 min. After cooling to below 70 °C, 50 mL of concentrated HNO3 solution was added. Then, the sample was refluxed for 30 min at  $\sim$ 95 °C without boiling again. The sample was evaporated to ~50 mL without boiling. After cooling to below 70 °C, 20 mL of Milli-Q water was added, followed by the slow addition of 100 mL of H<sub>2</sub>O<sub>2</sub> (30%). The solution was then heated until effervescence subsided. After cooling to below 70 °C, 50 mL of concentrated HCl solution and 100 mL of Milli-Q water were successively added. Then, the sample was refluxed for 15 min without boiling. After cooling to room temperature, the sample was filtered and diluted to 1000 mL using Milli-Q water. The aqueous dispersion of soil sample (20 mL) was further diluted with Milli-Q water (980 mL). Particulates in soil extract were removed by centrifugation at 16000 rcf for 10 min in a micro centrifuge before using.

## **Reference:**

- 1. R. A. Bryce, J. M. Charnock, R. A. D. Pattrick and A. R. Lennie, *J. Phys. Chem. A*, 2003, **107**, 2516–2523.
- 2. G. Senanayake, *Gold Bull.*, 2005, **38**, 170–179.
- 3. D. Feng and J. S. J. Van Deventer, *Hydrometallurgy*, 2002, **64**, 231–246.
- 4. A. C. Grosse, G. W. Dicinoski, M. J. Shaw and P. R. Haddad, *Hydrometallurgy*, 2003, 69, 1–21.
- 5. Y. Y. Chen, H. T. Chang, Y. C. Shiang, Y. L. Hung, C. K. Chiang and C. C. Huang, *Anal. Chem.*, 2009, **81**, 9433-9439.
- 6. G. Senanayake, *Miner. Eng.*, 2004, 17, 785–801.
- 7. L. H. Dubois and R. G. Nuzzo, *Rev. Phys. Chem.*, 1992, **43**, 437–463.
- 8. P. J. Renders and T. M. Seward, Geochim. Cosmochim. Acta, 1989, 53, 245–253.
- 9. P. Pyykko<sup>"</sup>, Angew. Chem., Int. Ed., 2004, **43**, 4412–4456.
- 10. P. Pyykko<sup>"</sup>, Inorg. Chim. Acta, 2005, **358**, 4113–4130.
- 11. G. Deschenes, R. Lastra, J. R. Brown, S. Jin, O. May and E. Ghali, *Miner. Eng.*, 2000, **13**, 1263–1279.
- 12. X. Y. Wang, C. G. Niu, L. J. Guo, L. Y. Hu, S. Q. Wu, G. M. Zeng and F. A Li, *J Fluoresc*, 2017, **27**, 643–649.
- 13. Y. J. Zhang, Y. M. Leng, L. J. Miao, J. W. Xin and A. G. Wu, *Dalton Trans.*, 2013, **42**, 5485-5490.
- 14. K. W. Huang, C. J. Yu and W. L. Tseng, Biosens Bioelectron, 2010, 25, 984-989.
- 15. D. R. Zhu, X. K. Li, X. Liu, J. N. Wang and Z. X. Wang, *Biosens Bioelectron*, 2012, **31**, 505-509.
- 16. C. Y. Li, Y. Zhou, Y. F. Li, X. F. Kong, C. X. Zou and C. Weng, *Anal. Chim. Acta*, 2013, 774, 79-84.
- 17. Z. Yu, W. Zhou, J. Han, Y. C. Li, L. Z. Fan and X. H. Li, *Anal. Chem.*, 2016, **88**, 9375-9380.